and then often in a mutilated form. From the appearance it looked as if the argon and the cadmium gas were entirely separated for the time being.

The reason for the appearance of the cadmium lines in the gas spectrum is difficult to account for. The main fact to be borne in mind is that these lines become visible even with the feeblest of currents, when the tube and the electrode are quite cold. The fact that they appear easily at pressures even as great as 60 mm. in the case of neon, differentiates the behaviour of the monatomic gases sharply from the diatomic gases; but why this should be so is not obvious. If the spectrum is due to small particles of metal at a high temperature which are torn from the cathode by the violent impact of positively charged gas ions, it is difficult to see why the same effect should not be produced by other gases, especially when the great range in the atomic weight of the inactive gases is remembered. Also, if this be the reason, it would seem probable that the whole of the spark spectrum of the metal would be seen at once, and not only certain lines depending on the nature and pressure of the gas in the tube.

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# *Further Experiments on Spontaneous Generation of Heat in Recently Hardened Steel.*

By Charles F. Brush, Sir Robert A. Hadfield, Bt., F.R.S., and S. A. Main, B.Sc.

(Received June 22, 1918.)

## *Introductory.*

The special interest for metallurgists of the phenomenon described in the title of this paper, particularly owing to the help it gives towards understanding the still rather obscure nature of the causes of hardening itself, encouraged the authors to carry out further work on lines suggested by the results of our previous experiments. The latter have been recorded in a previous paper,* which itself resulted from a still earlier paper† by one of us, in which the original discovery of the phenomenon was recorded.

This further work has added appreciably to our knowledge of the phenomenon and at the same time led to the discovery that, under certain conditions of quenching in which hardening does not take place, absorption instead of evolution of heat takes place.

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* 'Roy. Soc. Proc.,' A, vol. 93, p. 188.

† 'Proc. Am. Phil. Soc.,' vol. 54, No. 217 (May-July, 1915).

The paper is divided into two sections. The first, after a recapitulation of the previous work, describes and discusses the results of the new researches; in the second portion an empirical law is found which seems to regulate approximately the gradual diminution of the evolution of heat.

The experimental work is mainly confined to variation of heat treatment of one particular nickel chromium steel, though certain other materials have been examined.

The authors of the paper wish to mention how much indebted they have been to their assistants, Mr. T. H. Burnham, B.Sc., and Mr. W. J. Hall, B.Sc., A.R.C.S., for help so cheerfully rendered in the preparation of the paper during this time of war pressure.

### *Summary of Previous Researches.*

In the first paper* it was shown that a specimen of carbon tool steel, and also a specimen of "high-speed" tungsten-chromium steel after hardening by water quenching at a high temperature, spontaneously generated heat in appreciable quantity for at least several weeks, the rate of generation steadily diminishing. It was also shown that the carbon steel, after hardening, shrank progressively when tempered to "straw" colour, to "light blue" and finally annealed. It was further shown that another specimen of high-carbon steel, after hardening, spontaneously shrank in measurable amount for many days, the rate of shrinkage steadily diminishing. The plotted curve of spontaneous shrinkage was strikingly similar to a curve (not plotted) of total heat spontaneously generated in the other specimen of carbon steel, showing an apparent relationship between the two phenomena. But it was concluded that the mere contraction in volume could not be the prime cause of the spontaneous generation of heat observed, because calculations showed it to be wholly inadequate in amount. This conclusion was afterwards supported (second paper) in the cases of two specimens of nickel-chromium steel which, after quenching just above the temperature of decalescence, spontaneously generated heat freely but did not shrink at all.

The second paper,† after reviewing the first, treated principally of two specimens of Hadfield's nickel-chromium steel.

Each specimen consisted of 12 $\frac{1}{2}$-inch round bars 5 inches long, like in size and number to those of each of the steels of the first paper, so that the results obtained were quantitatively comparable with the earlier ones. Each specimen was first hardened by quenching at a temperature just above that of decalescence, as indicated by almost complete loss of magnetic susceptibility.

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* 'Proc. Am. Phil. Soc.,' vol. 54, No. 217 (May-July, 1915).

† 'Physical Review,' N.S., vol. 9, No. 3 (March, 1917); 'Roy. Soc. Proc.,' A, vol. 93, No. 649 (April 2, 1917).

For observing the magnetic behaviour of the steel while being heated or cooled in the gas furnace employed, the bundle of bars was surrounded by a single turn of asbestos-insulated platinum wire, the ends of which were connected with a ballistic galvanometer having the usual mirror and scale. The furnace was surrounded by a large coil of heavy copper wire, through which a direct electric current could be established and broken at will by means of a switch and storage battery. Before the steel bars were placed within the platinum loop inside the furnace, closure of the outer copper coil circuit caused a brief electric pulse in the loop and a "kick" in the galvanometer, giving a definite minimum deflection, easily observed with considerable precision. With the steel bars inside the platinum loop, the galvanometer deflection was, of course, many times greater, until, with rising temperature, the decalescence point was approached, then the deflection fell rapidly to the minimum value as above, or very near it. This simple induction apparatus was found entirely reliable and satisfactory.

Each of the nickel-chromium steels exhibited good generation of heat after hardening, as above.

They were again heated, to a temperature considerably above decalescence, and quenched as before. This second hardening induced a greater generation of heat than the first hardening, especially in the case of specimen B.

Specimen B was slowly heated a third time, somewhat above the temperature of complete loss of magnetic susceptibility, and allowed to cool very slowly in the furnace, until complete recovery of magnetic susceptibility was attained, then it was immediately quenched. A very fair generation of heat followed this treatment. This was quite unexpected, because it was thought that true hardening of the steel could not have taken place. In the absence of suitable apparatus, no test of hardness was at that time made. The 12 bars (specimen B) were next annealed by slowly heating to full decalescence, and then allowing to cool very slowly in the furnace. As expected, no trace of heat generation followed this treatment, which was made for checking purposes.

Before commencing the experiments with specimens A and B, a test-bar of each lot was prepared for accurate length measurements, which followed each treatment. The very interesting results of these measurements, differing materially in the two specimens, were tabulated and compared.

### *Continuation of the Research.*

The present paper deals with some later experiments, prompted by the anomalous behaviour of the specimen B of the Hadfield nickel-chromium steel after its third quenching, described above.

In conducting these experiments, an electric furnace was employed for heating, instead of the less convenient gas furnace formerly used, and the latest form of " scleroscope " for testing hardness was installed, also a most modern industrial thermo-electric pyrometer. The latter was used as it came from the maker, without further calibration, hence the temperatures recorded in this paper may be several degrees in error, though they are thought to be relatively consistent.

The apparatus employed in detecting, measuring, and following the progress of heat generation in the steels under treatment was fully described and illustrated in each of the former papers, and it is thought best to omit another description here.

It will be recalled that specimen B was left in the annealed condition. In this condition it was subsequently found to have a scleroscope hardness of 31. This is the mean of many consistent measurements. Each scleroscope hardness cited in this paper is the mean of at least 10 consistent measurements, each measurement made on a fresh spot of surface, carefully made smooth and flat.

In order to ascertain the critical temperature of decalescence and recalescence of specimen B, three of the 12 bars were gradually heated, until almost complete loss of magnetic susceptibility was reached. This occurred rather abruptly at about 777° C.* One of the bars was quenched at this temperature, and its scleroscope hardness was found to be 74. This may be taken as the probable hardness of specimen B after the first quenching, described in connection with the second paper.

The remaining two bars were allowed to cool very slowly in the furnace until complete recovery of magnetic susceptibility took place at about 660°. Recovery was abrupt in temperature. One of these bars was quenched at this temperature, and its hardness was found to be only 37, which is not much above annealed hardness (31). This would seem to indicate that true hardening did not take place in " specimen B " on its third quenching, already described above, although good spontaneous generation of heat followed the quenching.

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* An independent determination of this magnetic change-point, since made with a carefully calibrated pyrometer at Hecla Works, gave a temperature of 765°, indicating that at this point the pyrometer was reading 12° higher.

The three bars were again heated to complete decalescence and annealed in the furnace so as to leave all twelve bars of "specimen B" in annealed condition.

Fig. 1 is the curve sheet of specimen B. "Galvanometer deflection" measures temperature difference, indicated thermo-electrically, between the steel under examination and thermally equivalent quantity of water, contained separately in silvered Dewar vacuum jars. Both the steel and the water were usually brought to the same room temperature before being placed in the calorimeter; 55 scale divisions indicate a temperature difference of 1° C.

The curve of normal cooling runs out of the figure at the upper left-hand corner, and is easily distinguished from the others. This curve was obtained from a quantity of untreated steel equal in weight to specimen B, and warmed a few degrees above room temperature before being placed in the calorimeter. It shows the normal loss of heat due to imperfect thermal insulation alone, and is the basis of comparison for all the other curves. Obviously this curve may be plotted further to the right or left without impairing its validity; and it may be plotted to intersect any of the other curves at any desired point, to facilitate study of the other curve at or near the intersection. For the authors' convenience a metal template of the normal cooling curve was constructed and found most useful. Of course it is necessary that the base of the template be always kept coincident with the base line of the curve sheet.

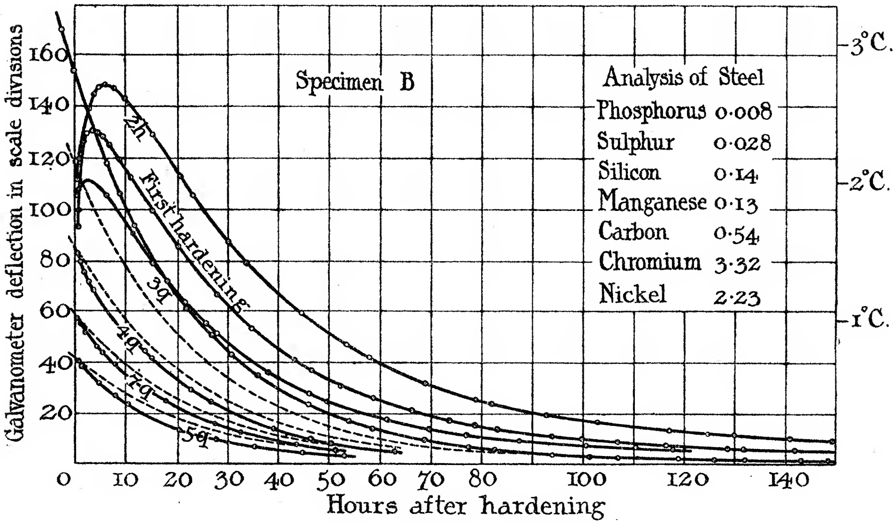

Fig. 1.

The curve of "first hardening" shows the spontaneous generation of heat which followed the first quenching at about 777°, the temperature of complete loss of magnetic susceptibility, after which the scleroscope hardness was probably about 74.

The curve of second hardening, indicated by "2 h," shows considerably greater generation of heat. Quenching temperature and hardness were not observed; but it is known that the quenching temperature was much higher than 777°.

The three curves thus far discussed were shown in the second paper already referred to, and the other curves here shown were subsequently plotted on the original curve sheet.

The third curve showing spontaneous generation of heat is indicated by "3 q," meaning third quenching (not hardening). To make it clear that heat was generated in this case, the curve of normal cooling has been drawn in a position for easy comparison (the upper dotted line). The "3 q" curve was described in the second paper but not plotted. The quenching temperature in this case must have been slightly below 660°, and probable hardness only about 37.

### *Experiments Showing Absorption of Heat.*

Specimen B left in the annealed condition at the close of former experiments, with a hardness of 31, was next gradually heated to 554°, allowed to cool slowly to 532° and quenched. It was then purposely brought to a temperature slightly above room temperature and placed in the calorimeter. The progress of cooling is plotted in the curve "4 q" (fourth quenching). For easy comparison the normal cooling curve is drawn as a dotted line through the first station of the "4 q" curve. Beyond this point the "4 q" curve lies everywhere below the normal cooling curve, showing conclusively that the steel cooled abnormally fast. In other words, there was spontaneous disappearance or absorption of heat in the steel, most notably during the first few hours after quenching. Hardness was 35·5.

The result of this experiment is remarkable, and was quite unlooked for. It was expected to find, if anything, a small generation of heat.

The steel was next heated to 562° and quenched. The result of this treatment is shown in the curve "5 q," with its own dotted normal cooling curve. Absorption of heat is again indicated, even greater than in "4 q," but somewhat differently distributed. Hardness was now 34·5.

Again the steel was heated, this time to 594°, and quenched. Again there was marked absorption of heat. The curve, "6 q," was almost identical with "4 q," and is not plotted, to avoid confusion of lines. Hardness was again 34·5.

The seventh heating was carried to 667° for quenching. This was a much larger temperature advance than in either of the preceding experiments, and was above the temperature of the third quenching, which was followed by very considerable generation of heat. But now there was very considerable absorption of heat, as shown in curve "7 q." Hardness was now 34.

### *Discussion of the Relative Conditions Bringing about Evolution or Absorption of Heat.*

It should be noted that the quenchings which were followed by absorption of heat were made at rising temperature which had not previously been exceeded (except slightly in the case of "4 q") since the steel was annealed. But in the case of third quenching the quenching temperature was a falling one, reached by cooling from the much higher temperature of decalescence. There is no apparent cause other than this for the radically different results of the third and seventh quenchings, which were made at substantially the same temperature. The temperature difference between complete loss and complete recovery of magnetic susceptibility, 117°, in this case is rather large; but, while this temperature drop, so far as can be judged by a duplicate experiment, brought about almost annealed softness and full restoration of magnetic qualities, it did not very greatly affect that quality of the steel, whatever it is, which is responsible for the spontaneous generation of heat. Seemingly, the unstable constituents of the steel which were formed at the critical temperature on heating did not have time to revert wholly to normal annealed condition while the metal was cooling to and passing through recalescence. The time of this cooling was about half an hour.*

To confirm the curious result of third quenching, *i.e.*, generation of heat without hardening, the bars were quenched the eighth time as follows:—Slowly heated (nearly two hours) to 819°, slowly cooled (nearly one hour) to 680° and quenched. During the heating complete loss of magnetic susceptibility occurred at 779°, which was an excellent confirmation of the former finding (777°). In cooling, full recovery of magnetic susceptibility came at 680°, which is 20° higher than before.†

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* Some allowance should, perhaps, be made for the fact that the magnetic change point, while very close in temperature to the "hardening" point in steel of this composition, is really a few degrees higher. When quenching just on the completion of the magnetic change, the carbon change may still be uncompleted, and a certain amount of stiffening, *i.e.*, partial hardening, with accompanying heat evolution, result. The results of the eighth quenching appear to confirm this view. Unfortunately, the hardness after the third quenching was not measured, and, owing to the critical nature of the quenching operation, the hardness figure obtained from a duplicate bar may not represent that after the original quenching.

† The temperature of the critical point on cooling is affected by the condition of heating and cooling, including the maximum temperature.

This higher quenching temperature may account for the somewhat greater hardness produced, which was later found to be 47, as against 37 for the third quenching (74 for true hardening above decalescence temperature).

Following the eighth quenching there was good generation of heat, better than after third quenching, but differently distributed in time—not so rapid at first, but much better sustained (curve not plotted). This appears to confirm the third experiment.

### *Résumé of Specimen B.*

Temperature of complete loss of magnetic susceptibility, 777° C.
" " recovery " " 660°–680°.

| | Quenching temperature. | Hardness. | Remarks. |
|---|---|---|---|
| First hardening ...... | About 777° C. | 74* | Good generation of heat. |
| Second " ...... | Much higher temperature | — | Much larger generation of heat. |
| Third quenching ...... | About 780°–660° | 37* | Fairly good generation of heat. |
| Annealing................ | — | 31 | |
| Fourth quenching ... | 554°–532° | 35·5 | Good absorption of heat. |
| Fifth " ... | 562° | 34·5 | " " " |
| Sixth " ... | 594° | 34·5 | " " " |
| Seventh " ... | 667° | 34 | " " " |
| Eighth " ... | 819°–680° | 47 | Good generation of heat. |

* Results obtained from a separate experiment.

Thus far, no promising explanation of the absorption of heat in the fourth, fifth, sixth, and seventh experiments has offered itself.

It may be seen that absorption was rapid during the first few hours, and greatly diminished at the end of 50 or 60 hours; while generation was well marked up to 150 hours. In earlier experiments generation of heat was well marked up to 150 hours. In earlier experiments generation of heat was easily detected at the end of a month.

### *Experiments with Carbon Steel.*

As it seemed desirable to learn whether plain carbon steel would show, like the nickel-chromium steel, generation of heat without true hardening, or absorption of heat when quenched at rising temperatures below the lower critical temperature, after annealing, the following experiments were made with the carbon steel used for the first experiment described in the first paper of the series. The normal cooling curve and upper curve of heat generation shown in fig. 2 are taken from that paper.

Following is a *résumé* of the early and recent experiments with the carbon steel:—

1st (original) hardening.—Quenched at very high temperature. Temperature and hardness not then observed.

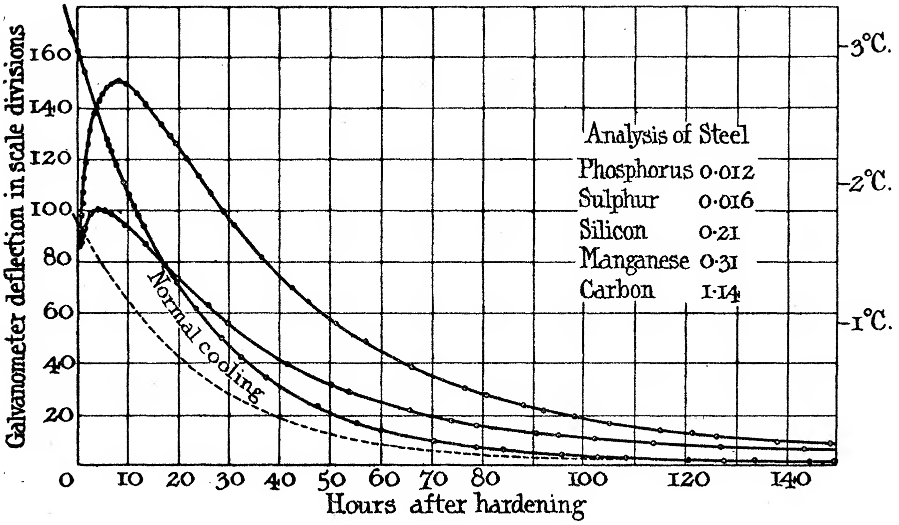


Fig. 2.

Large generation of heat, as shown in upper curve of fig. 2. Scleroscope hardness, recently observed, 79.

2nd (recent) hardening.—Quenched at 802°, considerably above decalescence, but much lower than in first hardening.

Complete loss of magnetic susceptibility occurred at 765°. Good generation of heat but very much less than in 1st, as shown by the lower curve of fig. 2. For convenient comparison with this curve the normal cooling curve is shown as a dotted line appropriately located.

Hardness was now 73.

3rd quenching.—Heated to 815°, somewhat above preceding quenching temperature, allowed to cool slowly to 720° and quenched.

This was a *little below* the temperature of complete recovery of magnetic susceptibility, which had occurred at 729°.

Hardness was now only 28·5, and there was *no generation of heat.*

(The nickel-chromium steel had shown good generation of heat under similar circumstances.)

Note the small temperature difference, 36° in this case, between complete loss and complete recovery of magnetic susceptibility.

Annealed by heating to 822°, to obliterate previous quenching effects, and cooling slowly in furnace.

Hardness was now 25·5.

4th quenching.—Heated slowly, from annealed condition, to 633° (considerably below the lower critical temperature) and quenched.

Hardness was again 28·5, and there was *no trace of absorption of heat.*

(The nickel-chromium steel had shown good absorption of heat under similar circumstances.)

5th quenching.—Heated slowly to 732°, just above the temperature of complete recovery of magnetic susceptibility, and quenched.

No generation or absorption of heat, nor change in hardness (28·5).

Clearly, the carbon steel showed none of the eccentricities of the nickel-chromium steel when quenched below the hardening temperature; but when quenched a little above, as well as far beyond this temperature, they behaved very much alike.

### *Experiments with White Iron.*

While considering plain carbon steel, it was thought worth while to observe heat generation in some white cast iron, very high in combined carbon, and very pure otherwise, which was conveniently at hand.

Fig. 3 shows the composition of this metal, which is hard and very brittle. The carbon is all combined, and remains so after heating and quenching.

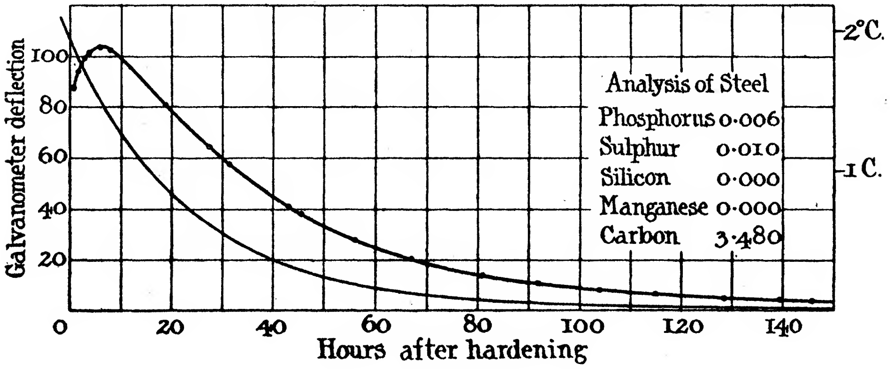


Fig. 3.

An induction experiment with a large lump of the metal showed—

Temperature of complete loss of magnetic susceptibility, 757°.
„ „ recovery „ „ 704°.

Slowly heated many fragments, aggregating in weight that of the usual 12 bars of steel, to 906° and quenched.

Very moderate generation of heat followed the quenching, as shown in fig. 3, and it was much less persistent than usual, as indicated by its small value at the end of 150 hours. Hardness was 76.

The behaviour of this specimen of white cast iron was not thought sufficiently encouraging to warrant further experiments with it.

### *Experiments with Swedish Charcoal Iron.*

For a general check on the performance of the apparatus, 12 ½-inch round bars of Swedish charcoal iron, of the aggregate weight of the steel usually employed, were slowly heated to 960° and quenched. Complete loss of magnetic susceptibility had occurred at 801°. The bars were warmed about 3° just before being placed in the calorimeter.

There was no trace of heat generation following the quenching. Indeed, the curve of cooling followed the normal cooling curve with such fidelity that nowhere did they differ as much as the width of the curve line. This was very gratifying in view of the fact that observations for the normal cooling curve were more than two years ago, and checked only once since that time. Hardness was 18·5.

Again heated above decalescence and annealed by cooling in the furnace.

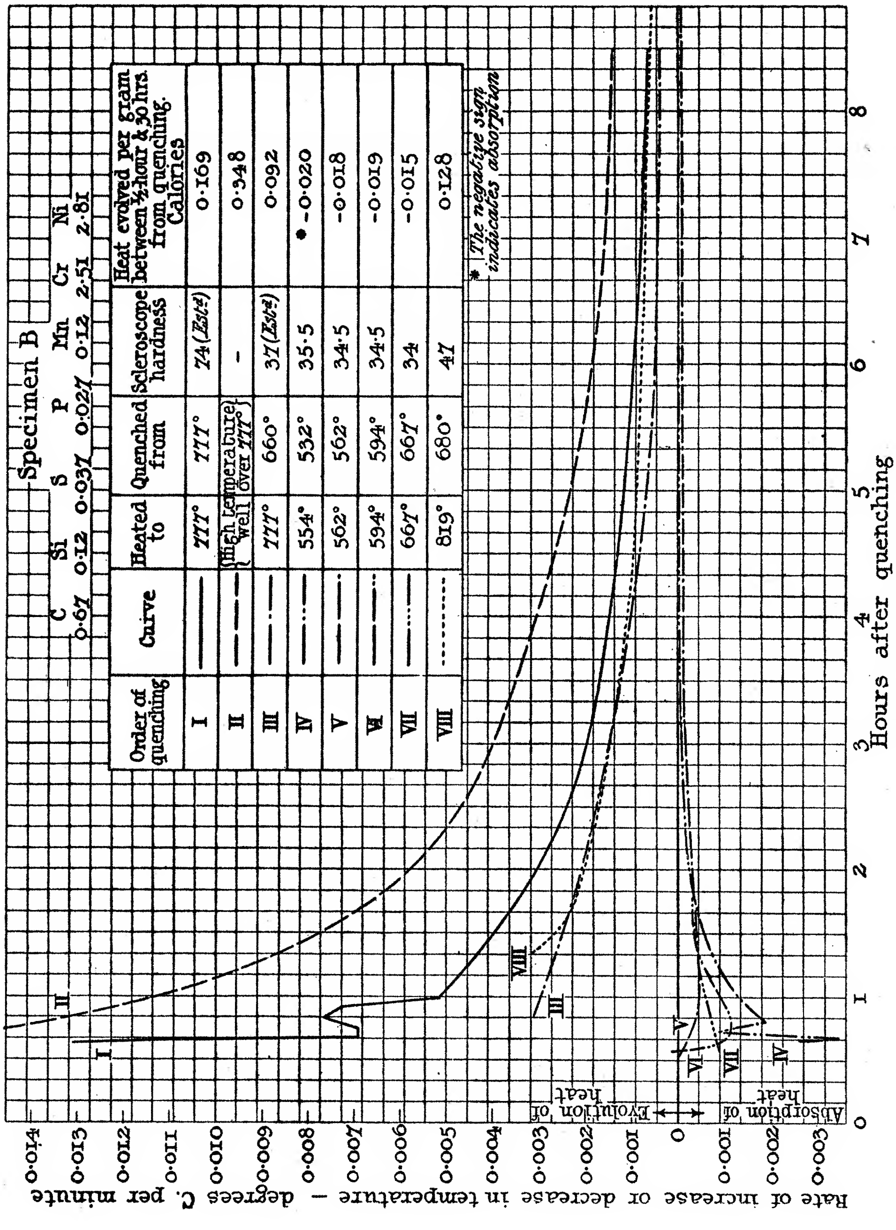
Hardness remained 18·5, showing that the previous heating and quenching had no effect whatever on the hardness of this, presumably, very pure iron.

### *Attempts to Discover the Mathematical Law Regulating the Evolution and Absorption of Heat.*

As a further step towards elucidating the cause of these phenomena, it was considered desirable to obtain a more precise idea of the rate of evolution (or absorption) of heat and its progress with time. The laboratory observations of the experiments on the nickel-chromium steel specimen "B" were, therefore, carefully examined.

The observed changes of temperature were corrected by observing the normal rate of cooling due to excess of temperature of the specimen over its surroundings and applying the correction. Tables were prepared giving, at short intervals, the corrected absorption or evolution of heat in successive quenchings. The results are plotted for the first nine hours in fig. 4.

The corrected curves of heat evolution or absorption shown on these diagrams give a better idea of the relative magnitude and progress of the heat evolution or absorption under the various quenching conditions than can be gathered from the time-temperature curves shown in fig. 1. For example, these curves prove that the evolution or absorption of heat has its greatest intensity immediately after quenching, after which it continuously decreases, although at first sight it might appear from figs. 1 and 2 that the heat evolution at first increases, reaches a maximum, and then decreases.



Specimen B

| C | Si | S | P | Mn | Cr | Ni |
|---|---|---|---|---|---|---|
| 0·67 | 0·12 | 0·037 | 0·027 | 0·12 | 2·51 | 2·81 |

| Order of quenching | Curve | Heated to | Quenched from | Scleroscope hardness | Heat evolved per gram between ½-hour & 30 hrs. from quenching. Calories |
|---|---|---|---|---|---|
| I | ——— | 777° | 777° | 74 (*Estd.*) | 0·169 |
| II | — — — | (High temperature well over 777°) | | – | 0·348 |
| III | —·— | 777° | 660° | 37 (*Estd.*) | 0·092 |
| IV | —··— | 554° | 532° | 35·5 | * –0·020 |
| V | —·—·— | 562° | 562° | 34·5 | –0·018 |
| VI | ——··· | 594° | 594° | 34·5 | –0·019 |
| VII | —···— | 667° | 667° | 34 | –0·015 |
| VIII | ········· | 819° | 680° | 47 | 0·128 |

* *The negative sign indicates absorption*

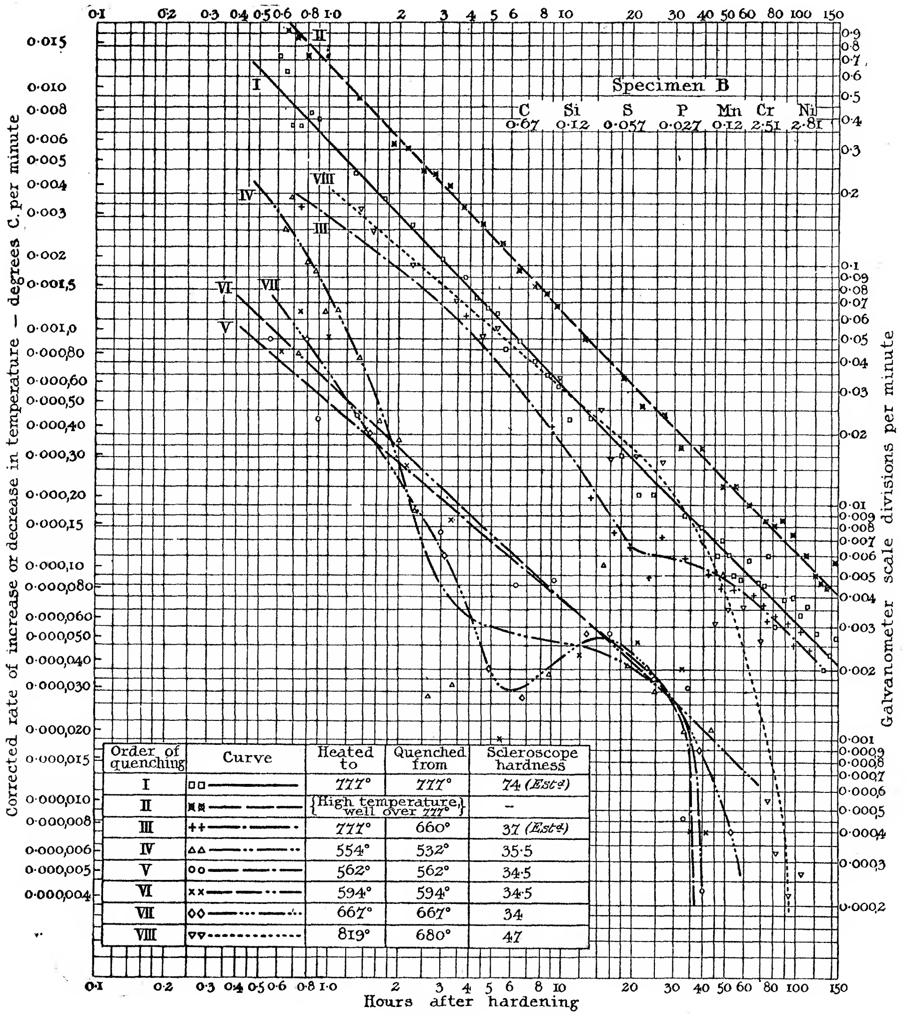
Fig. 4.

*Rate of Heat Evolution and Absorption.*

Down to the present, although it is known that the heat evolution or absorption has its greatest activity immediately after quenching, and thereafter steadily diminishes, nothing has been determined as to its rate of decay.

It is important to know this, in forming or deciding on any theory to account for the phenomena.

To determine this rate of decay, the curves of fig. 4 were re-plotted on logarithmic paper (fig. 5). The curves, whether of evolution or absorption, now all have a general slope downwards approximating to 1 in 1.

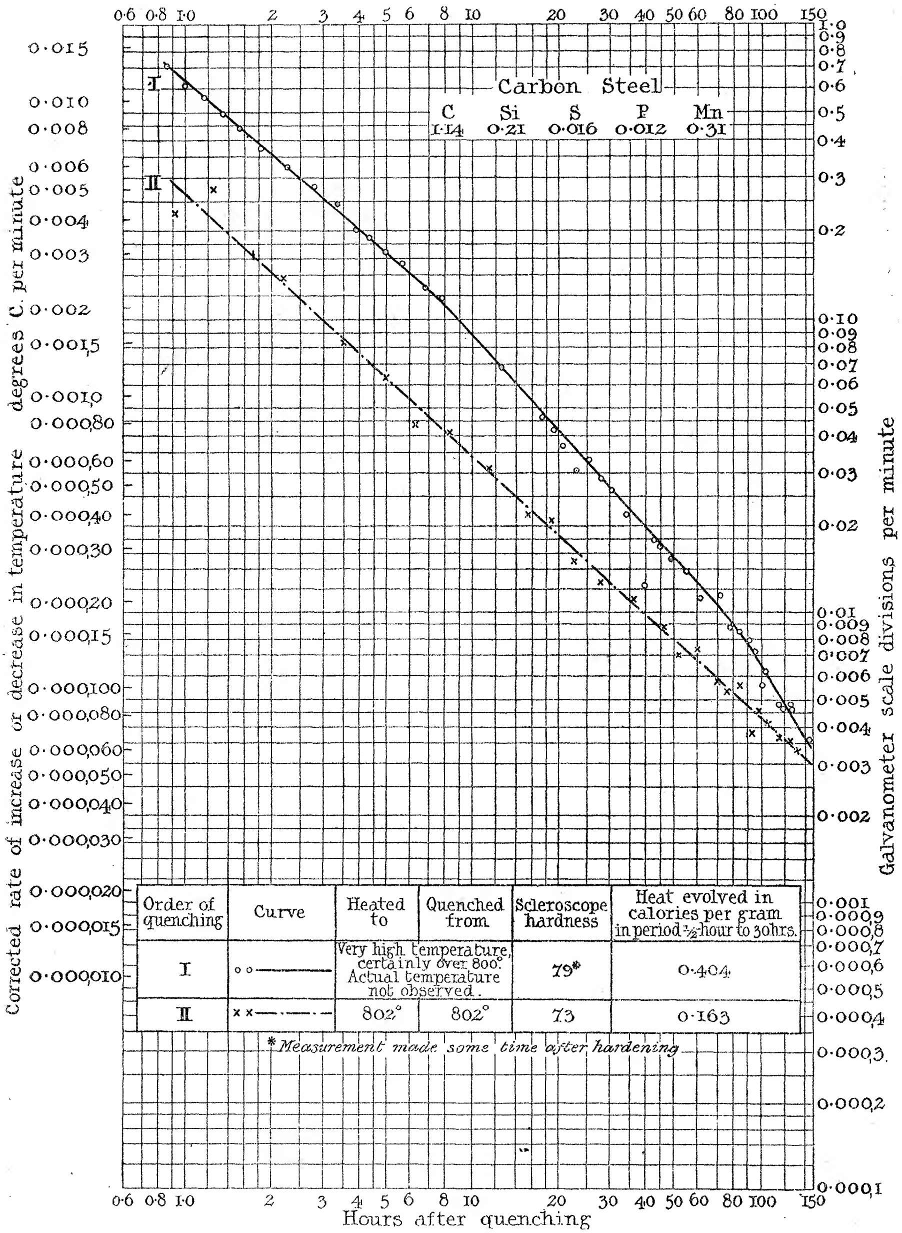


| Order of quenching | Curve | Heated to | Quenched from | Scleroscope hardness |
|---|---|---|---|---|
| I | □□ ——————— | 777° | 777° | 74 (*Estᵈ*) |
| II | ⌧⌧ —— —— —— | {High temperature, well over 777°} | | – |
| III | ++ ——·——· | 777° | 660° | 37 (*Estᵈ*) |
| IV | △△ ——··——·· | 554° | 532° | 35·5 |
| V | ○○ —— ——·—— | 562° | 562° | 34·5 |
| VI | ×× —— ——··—— | 594° | 594° | 34·5 |
| VII | ◇◇ ——···——·.· | 667° | 667° | 34 |
| VIII | ▽▽ -------------- | 819° | 680° | 47 |

FIG. 5.

This seems to show that the activity of the evolution (or absorption) of heat diminishes in inverse ratio to the time elapsed since the specimen was quenched—after 10 hours it has dropped to only one-tenth of its value one hour after quenching—after 100 hours (or just over four days) only one-hundredth, and so on.

What is true only approximately for the curves in general is almost precisely correct for the first and second quenchings, which are the only cases in which true or complete hardening took place. For these, the straight line with a slope of 1 in 1 is really the best line which could be drawn to fit the numerous observations.



| Order of quenching | Curve | Heated to | Quenched from | Scleroscope hardness | Heat evolved in calories per gram in period ½-hour to 30 hrs. |
|---|---|---|---|---|---|
| I | o o ——— | Very high temperature, certainly over 800°. Actual temperature not observed. | | 79* | 0·404 |
| II | × × —·—·— | 802° | 802° | 73 | 0·163 |

*Measurement made some time after hardening.

FIG. 6.

Similar curves (fig. 6) plotted for a specimen of carbon steel agree generally with the above, the average slope for the first quenching being very closely 1 in 1, but for the second quenching the rate of evolution of heat does not die off quite so rapidly.

It may be taken therefore as a good approximation that the activity of the evolution (or absorption) of heat is measured by:

$$\text{Rate of evolution} \times \text{time after quenching} = \text{a constant.}$$

This law cannot, however, represent the facts completely, either at the beginning or the end of the period of evolution of heat, as it would give an infinite development of heat.

To give a more practical idea of the magnitude of the heat evolution, this has been expressed in two different ways in the following Table for the nickel-chromium steel, second quenching :—

| Time after quenching. | Horse-power per ton. | Converted into mechanical energy, the heat evolved would lift the steel at the rate of |
|---|---|---|
| h. m. | | |
| 0 1 | 8·1 | 120 feet per minute. |
| 0 15 | 0·54 | 8 ,, ,, |
| 0 30 | 0·27 | 4 ,, ,, |
| 1 0 | 0·135 | 2 ,, ,, |
| 12 0 | 0·011 | 2 inches per minute. |
| Days. | | |
| 1 | 0·0056 | 1·0 inch per minute. |
| 2 | 0·0028 | 0·5 ,, ,, |
| 4 | 0·0014 | 0·25 ,, ,, |
| 7 | 0·0008 | 0·14 ,, ,, |
| 30 | 0·00018 | 0·03 ,, ,, |

It will be understood that the figures given for times less than 30 minutes or more than seven days (being outside the actual experimental period) are estimates.

This Table brings out in a striking manner the magnitude of the heat evolution just after quenching. For the carbon steel specimen they are even larger.

### *Calculations of the Quantities of Heat Evolved or Absorbed.*

It is not possible on present data to form an estimate of the total amount of heat evolved or absorbed. Such an estimate is, however, possible for a specified period of time, and it is useful to determine this because, the heat evolution falling off in all cases in approximately the same ratio, the figures obtained will be approximately in the same ratio as the total quantities of heat evolved.

Worked out for the period of time from half-an-hour after quenching to 30 hours after quenching, the figures for the various quenchings are as follows :—

| Quenching. | Heated to | Quenched from | Scleroscope hardness. | Calories per gramme of steel. | Foot-lbs. per lb. of steel. |
|---|---|---|---|---|---|
| | | | Nickel-chromium steel "B." | | |
| I | 777° | 777° | 74 (estd.) | 0·169 | 235 |
| II | (High temperature, well over 777°) | | — | 0·348 | 484 |
| III | 777° | 660° | 37 | 0·092 | 128 |
| IV | 554° | 532° | 35·5 | −0·020 | 27·8 |
| V | 562° | 562° | 34·5 | −0·018 | 25 |
| VI | 594° | 594° | 34·5 | −0·019 | 26·4 |
| VII | 667° | 667° | 34 | −0·015 | 20·8 |
| VIII | 819° | 680° | 47 | 0·128 | 178 |
| | | | Carbon steel. | | |
| I | (Very high temperature, certainly over 800°) | | 79 | 0·404 | 561 |
| II | 802° | 802° | 73 | 0·163 | 227 |

The negative sign signifies absorption.

From this numerical comparison, it will be seen that the heat evolved varies considerably according to the method of quenching, being 60 per cent. less in Experiment VIII than in Experiment II.

In the case of the carbon steel, quenched from well over 800° C., which shows the largest heat evolution of all, the heat evolved is sufficient to lift the steel through a height of no less than 560 feet. This is only a portion of the total quantity. In the first half-hour after quenching, probably an even larger quantity was evolved, and, after 30 hours have elapsed, the quantity still to be evolved is also probably very considerable.

The absorptions of heat are all more or less equal in magnitude, and only about 5 per cent. of the maximum amount of heat evolved from the same steel in Experiment II.

### *Evolution of Heat Due to Spontaneous Contraction.*

In a previous paper by one of us,[*] it was shown that, simultaneously with the evolution of heat in a specimen of new hardened carbon steel, a steady contraction took place, the amount of which was determined.[†]

Such contraction in itself accounts for a certain evolution of heat, in the same way as the heat of the sun has been attributed to its continual contraction (in that case due to gravitation).

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[*] C. F. Brush, "Spontaneous Generation of Heat in Recently Hardened Steel," 'Proc. Am. Phil. Soc.,' vol. 54, No. 217.

[†] Fig. 6, *loc. cit.*

It was concluded that contraction, while contributing to the heat actually evolved, could not at all adequately account for it.

The further calculations which follow, while confirmatory on this point, are of interest, as they are based on different data, and probably give a better idea of the proportion due to contraction.

At the top of fig. 7 is re-plotted the contraction diagram for the carbon steel above referred to, on semi-logarithmic paper. The curve now becomes practically a straight line

$$C_l = 159 \log_{10} T + 134,$$

where $C_l$ is the linear contraction in millionths of the original length after T hours.

Recent experiments* have shown that, under fluid pressure exerted all over the exterior surface, all steels (which, however, do not appear to have included hardened steel), except in a few special cases have closely the same degree of compressibility. For 10,000 atmospheres the volume compression was 1 per cent.

From this it may be calculated that the energy required to compress 1 grm. of steel by 1 per cent. of its volume is 0·313 expressed in calories.

The actual volume contraction of the carbon steel specimen in the period one half-hour after quenching to 30 hours after quenching was 0·0848 per cent. by volume (fig. 7).

The amount of heat evolved in each gramme of steel due to contraction in this period is therefore

$$0{\cdot}0848 \times 0{\cdot}313 = 0{\cdot}0266 \text{ calories}$$

(sufficient to raise the steel mechanically through 37 feet).

Comparing this with the actual quantities of heat evolved by the carbon steel (fig. 6), which were 0·404 and 0·163 for the two quenchings, it is confirmed that contraction is not by any means the sole cause of the heat evolution.

The rate of contraction is given by

$$\frac{dCv}{dT} = \frac{3{\cdot}45}{T}.$$

The rate of evolution of heat due to contraction is proportional to this, and is, therefore, like the actual evolution of heat, in inverse ratio to the time elapsed.

This suggests that a slow change goes on in the steel for a considerable time after quenching, and that both the evolution of heat and contraction are results of this change.

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* Day and Sosman, "Some High-Pressure Phenomena," 'Engineering,' August 3, 1917, p. 124.

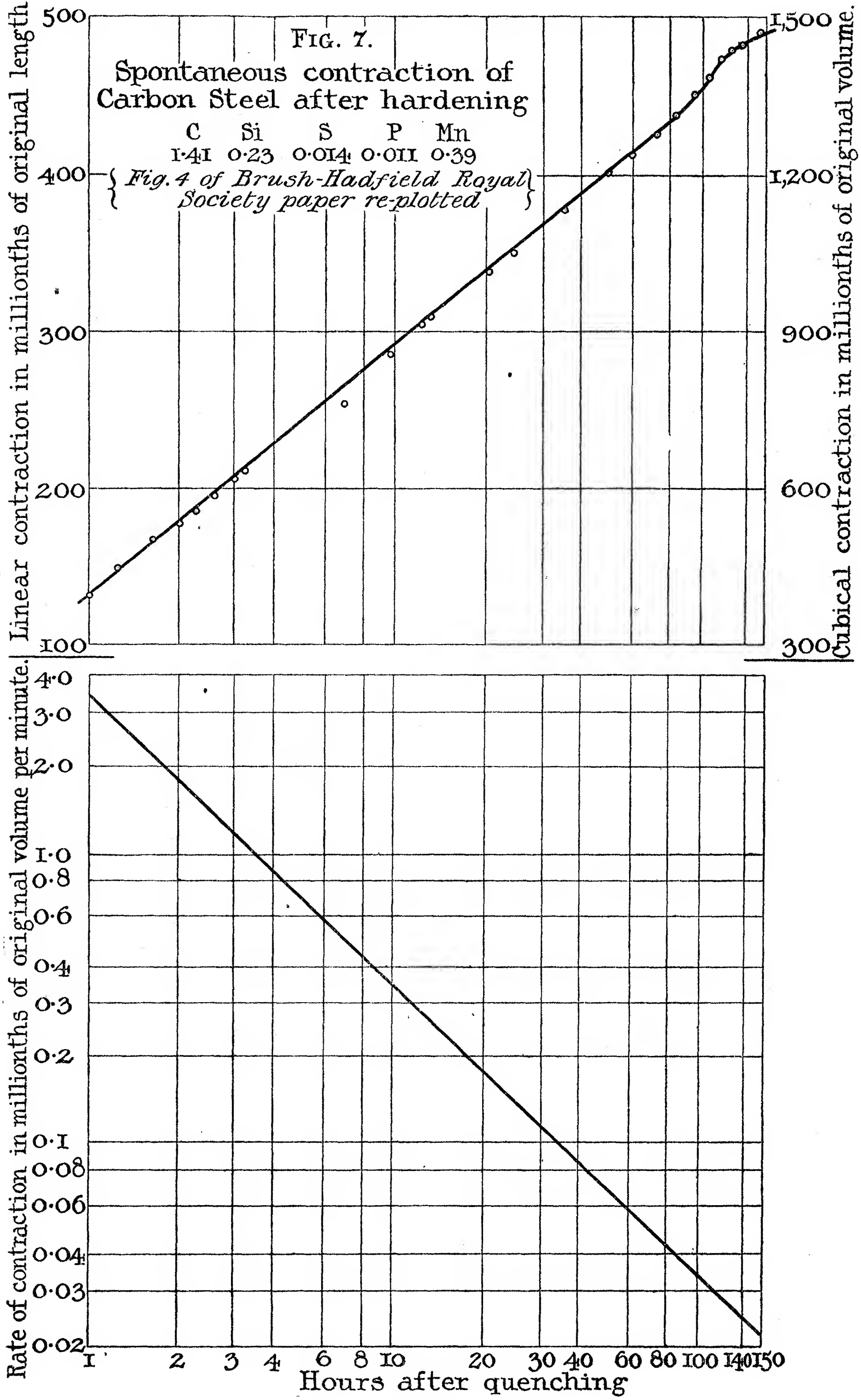
Fig. 7.
Spontaneous contraction of Carbon Steel after hardening
C Si S P Mn
1·41 0·23 0·014 0·011 0·39
*Fig. 4 of Brush-Hadfield Royal Society paper re-plotted*
Linear contraction in millionths of original length.
500
400
300
200
100
Cubical contraction in millionths of original volume.
1,500
1,200
900
600
300
Rate of contraction in millionths of original volume per minute.
4·0
3·0
2·0
1·0
0·8
0·6
0·4
0·3
0·2
0·1
0·08
0·06
0·04
0·03
0·02
1
2
3
4
6
8
10
20
30
40
60
80
100
140
150
Hours after quenching

Fig. 7.

### *Résume.*

To sum up the chief points of the second paper:—

(1) The rate of evolution or absorption of heat by quenched steel is, after a short initial period, approximately in inverse ratio to the time elapsed after quenching.

(2) The actual rate of evolution has been determined for various specimens.

(3) The rate of contraction of quenched steel was found to follow the same law as the rate of evolution or absorption of heat.

(4) This suggests that the contraction is intimately connected with the heat evolution, both being due to the same cause.

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# *Sounds Produced by Drops Falling on Water.*

By A. Mallock, F.R.S.

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[Plate 1.]

I had long been interested in the various musical sounds which falling drops produce when they strike the surface of water, and in 1915 I made some experiments on the subject which are perhaps worth recording.

The sounds, of course, last for a very short time, and to hear them well other noises should be absent. Drops after a shower falling from leaves overhanging a sheltered pond, or the dripping from a tap in a cistern, are some of the commonest examples in which the musical character of the sound can be well distinguished. On listening attentively it will be noticed that pitch of the note is high at first, then falls and afterwards again rises. The duration of the sound is so short that it is difficult to estimate the actual pitch, but the lowest part of the sound was the most characteristic.

It seemed probable that the pitch would be dependent on the resonance of the cavity formed by the impact of the falling drop, and the experiments here described were made with the object of determining the magnitude and shape of the cavity in question.

It was found by trial that the same class of sounds were produced whether the falling body was a liquid drop or a solid sphere. The experiments, therefore, were made with solid spheres, as there is less complexity in the